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(71)Applicant : MITSUBISHI ELECTRIC CORP

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(72)Inventor : UCHIKAWA HIDEFUSA

MAEKAWA TAKESHI

NOZAKI AYUMI

MIYASHITA SHOJI

(54) POSITIVE ELECTRODE ACTIVE MATERIAL, ITS MANUFACTURE AND LITHIUM ION SECONDARY BATTERY USING POSITIVE ELECTRODE ACTIVE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To manufacture active material for a lithium secondary battery having excellent performance at a low cost by effectively using ferrite.

SOLUTION: In a method for manufacturing positive electrode active material, a solution is obtained by mixing a solution dissolved with a composite oxide (ferrite) containing mainly a composition expressed by AF₂O₄ (wherein A represents Mn, Fe, Zn, Co, Ni or Cr), an inorganic salt including a lithium ion, an inorganic salt including an ion of Co, Ni, Mn or Fe (a transition metal element) and a complexing agent for forming a complex of lithium with the transition metal element in a ratio of the lithium ion to the transition metal element ion being 1:x (0.5≤x≤1.0). Subsequently, a solvent of the solution is removed by atomizing and drying, thereby producing a precursor. Thereafter, the precursor is subjected to heat treatment.

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 CLAIMS

[Claim(s)]

[Claim 1] The following general formula AFe_2O_4 (the inside of a formula and A are Mn, Fe, Zn, Co, nickel, or Cr)

The solution which dissolved the multiple oxide which comes out and makes a principal component composition shown, and the mineral salt containing a lithium ion, The mineral salt containing the metallic element ion of ** a kind of 1st at least of Co, nickel, Mn, and the Fe(s), The process which obtains the solution which mixed a lithium and the 1st metallic element of the above, and the complexing agent that forms a complex so that the ratio of a lithium ion and the metallic element ion of the above 1st might be set to 1:x ($0.5 \leq x \leq 1.0$), The manufacture method of the positive active material which gives the process which removes the solvent of the above-mentioned solution by spray drying, and obtains a precursor, and the process which heat-treats the above-mentioned precursor.

[Claim 2] The manufacture method of a positive active material according to claim 1 that the mineral salt containing a lithium ion is characterized by being a lithium nitrate, lithium sulfate, a lithium chloride, lithium fluoride, an acetic-acid lithium, or a lithium hydroxide.

[Claim 3] The manufacture method of a positive active material according to claim 1 or 2 that the mineral salt containing the 1st metallic element ion is characterized by being a nitrate, a sulfate, a chloride, acetate, a fluoride, or a hydroxide.

[Claim 4] The manufacture method of a positive active material according to claim 1 to 3 that a complexing agent is characterized by being oxalic acid, a tartaric acid, a citric acid, a succinic acid, a malonic acid, or a maleic acid.

[Claim 5] The positive active material with which it is obtained by the manufacture method according to claim 1 to 4, and a principal component is indicated to be by the following general formula LiM_xO_2 (M is Co, nickel, Mn, or Fe among a formula, and it is $0.5 \leq x \leq 1.0$).

[Claim 6] The positive active material from which the principal component was obtained by the manufacture method according to claim 1 to 4 using the multiple oxide which are $CoFe_2O_4$ and $NiFe_2O_4$.

[Claim 7] The positive active material from which the principal component was obtained by the manufacture method according to claim 1 to 4 using the multiple oxide which is $MnFe_2O_4$.

[Claim 8] The rechargeable lithium-ion battery characterized by the above-mentioned positive-active-material layer having the positive active material of either a claim 5 or the claim 7 in the rechargeable lithium-ion battery equipped with the separator holding the nonaqueous electrolyte containing a lithium ion between the positive-active-material layer, the negative-electrode active material layer, and the above-mentioned positive electrode and a negative-electrode active material layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the positive active material used in the rechargeable lithium-ion battery which used the nonaqueous solution as the electrolyte, its manufacture method, and the rechargeable lithium-ion battery using this.

[0002]

[Description of the Prior Art] In recent years, the miniaturization of a cellular phone or electronic equipment called a personal digital assistant progresses, and the cell used for these devices is also asked more for the property of the high voltage and twist high capacity. Then, it has a great hope for the rechargeable lithium-ion battery which used the nonaqueous solution with a large ejection capacity per unit weight as the electrolyte, and development is furthered in every direction.

[0003] The stratified compound a lithium can be taken in and out of which electrochemically is used for the positive active material of this rechargeable lithium-ion battery, and LiCoO_2 , LiNiO_2 , LiFeO_2 , or LiMn_2O_4 etc. whose general formula of an active material is the multiple oxide of $\text{Li}\alpha\text{O}_2$ ($0.5 \leq \alpha \leq 1.0$), i.e., a lithium and transition metals which are generally expressed with $\text{Li}\alpha\text{O}_2$ or $\text{Li}\alpha_2\text{O}_4$ (α is a transition-metals element), is used.

[0004] Usually, the above-mentioned multiple oxide mixes compounds, such as lithium compounds, such as a lithium carbonate and a lithium oxide, and transition-metals oxides, such as nickel oxide, cobalt oxide, and manganese dioxide, a hydroxide, by the predetermined ratio, and is obtained by calcinating this at the temperature of 700-900 degrees C in the atmosphere or oxygen for 1 hour to several hours as shown in for example, U.S. JP,4302518,B or U.S. Pat. No. 4980080.

[0005] Moreover, there is an example which has added the element [minute amount / Ti / aluminum,] / as shown in ZrO_2 and the LiNi_2Co_2 -publication-number No. 242891 / five to / official report which combined these multiple oxides, and which are composition as indicated by the Provisional-Publication-No. No. 299056 / 63 to / official report for the purpose of a capacity rise, improvement in a charge-and-discharge cycle property, etc. Thus, there are very many examples of a proposal as additional trace elements.

[0006] However, practical use is presented only LiCoO_2 from which it is comparatively stabilized and high capacity is obtained in these active materials now, and there is room of an improvement in geometric capacity far still more.

[0007] This active material mixes cobalt compounds, such as lithium compounds, such as a lithium carbonate, and a lithium oxide or a lithium hydroxide, cobalt oxide, or cobalt hydroxide, to dry type, and is obtained by calcinating this at the elevated temperature of about 900 degrees C. Although it is compounded in many cases by the usual dry process since it is comparatively easy to compound this multiple oxide, when a limitation is in homogeneous mixture in dry process, especially a lithium compound with small specific gravity and a transition-metals compound with large specific gravity are mixed with dry process, it is difficult to mix to homogeneity because of a specific gravity difference. This heterogeneity in the end of mixed powder becomes the heterogeneity of an active material crystal,

and the cause of a defect, and cell capacity falls by barring movement of the lithium ion in the layer structure of an active material. Moreover, the portion of these disorders has the unstable layer structure, and since the bonding strength between layers is weak, a layer structure is destroyed with receipts and payments of a lithium ion, and it becomes the cause by which the repeat property of charge and discharge deteriorates. From the above thing, the above-mentioned multiple oxide obtained by the above-mentioned conventional manufacture method had the room of an improvement in geometric capacity far still more.

[0008] Then, in order to carry out homogeneous mixture of each element which constitutes an active material, the salt of a lithium compound and the salt of a transition-metals compound are melted in water, it considers as solution, and the attempt of the wet method mixed by the ionic state is made. For example, the salt of nickel or a lithium is dissolved in a suitable solvent, it mixes by wet [so-called], and there is a method of calcinating this and obtaining an active material as indicated by the publication-number No. 325966 [five to] official report, and the publication-number No. 44970 [six to] official report.

[0009] Although a lithium and transition metals are mixed very homogeneously in solution in these examples since it is mixed in the state of ion, in case a solvent, for example, water, is removed, a homogeneous state will not be held, but the salt which segregated with the anion kind which lives together will be formed, each component will dissociate and exist, and obtaining the homogeneous target precursor has the problem of being very difficult.

[0010] In order to solve this problem, the method (complex polymerization method) of adding the cation which exists in the method (coprecipitation method) of producing the coprecipitation salt which adds a suitable precipitant and consists of two or more ion, or a solution, and a complexing agent which forms a compound complex, and obtaining a precursor etc. is examined. A lithium ion and transition-metals ion make coprecipitation and a compound complex from carrying out like this both cations and here, consequently it is known that the homogeneity of ion mixture in the state of a precursor can be held. For example, after adding ethylene glycol in a publication-number No. 203834 [six to] official report at a lithium and the acetate of transition metals and forming a compound alcoholate, it is made to gel, and the method of making the salt of a lithium compound and the salt of a transition-metals compound gel with citric-acid solution in the method of calcinating this and obtaining an active material, a publication-number No. 163046 [six to] official report, and a publication-number No. 142065 [seven to] official report, calcinating them in them, and obtaining an active material etc. is indicated

[0011] However, in the coprecipitation method of the above-mentioned former, it is difficult to produce precipitation difficultly and separately theoretically and to attain the homogeneity of precipitate by this method to make an element which chemical property, such as alkali-metal ion and transition-metals ion, is large, and is different coprecipitate.

[0012] A means to remove a solvent from a compound complex poses a problem by the latter complex polymerization method. It becomes a precursor lacking in the homogeneity which is not necessarily maintained in case, as for this state, a solvent is removed, although the complex ion in which two or more element [inside / of a solution] ion formed the complex when using various complexing agents may exist, and does not change at all with dry process as a result in many cases. Although the polycondensation reaction is advanced by removing the solvent gradually at the reaction with the above-mentioned ethylene glycol or a citric acid Very long time is required for a reaction, and it will remelt with the moisture which was not able to remove the once generated gel, or the moisture in air, since the anion and salts which live together, such as an acetic-acid solution and a nitric-acid solution, are formed and it deposits, gap of composition will arise, and the special homogeneity attained by the complex will be spoiled. Moreover, these wet methods with which water may remain in the stage of a precursor are not suitable for composition of an active material whose this invention dislikes water to a degree very much like the target active material. Furthermore, since these are all the reactions accompanied by gelling, it becomes ***** gel, and hygroscopicity is high, handling becomes bad, and the precursor obtained has a big problem in the handling of gel. Moreover, since these methods need a lot of coprecipitaters and complexing agents, such as ethylene glycol, and moreover pass through complicated

manufacturing processes, such as reduced pressure drying, they have the problem that there is little yield of a precursor. Although these methods may be suitable for powder manufacture of particular application, they cannot be called realistic synthetic method of the active material which needs an amount for a cell use.

[0013] On the other hand, the spray drying method is learned as one of the powder composition methods of other. Although this method is used in many cases for the purpose of a granulation, there is also a report as the synthetic method of an active material. For example, as indicated by the publication {Solid State Ionics 44(1990) pp.87-97} After mixing the powder of LiOH solution and nickel (OH)₂ as a synthesis method of LiNiO₂ and considering as a slurry, As indicated by the example which produces and calcinates the precursor which carried out the coat of the front face of the powder of nickel (OH)₂ by LiOH by carrying out spray drying of this, and obtains an active material, and the publication-number 2-No. 9722 official report The solution of a manganese compound and a lithium compound is sprayed using a supersonic humidifier as the manufacture method of manganic acid ghost powder, and there is an example which calcinates this and obtains an active material. However, these are not the active material synthesis methods which are used as the coat and the solvent removal method on the front face of a particle, and were excellent in mass production. Moreover, the precursor obtained from the solution of only a raw material component has very high hygroscopicity, and a problem is in the handling.

[0014] That is, the solution composition which can obtain a precursor, applying an advantageous wet method compared with dry process in respect of homogeneity, and maintaining the homogeneous mixed state in the solution of active material composition further in order to obtain a highly efficient active material, and the removal method of a solvent become very important. Then, when the method (international public presentation official report WO 98/29915) of obtaining an active material, with the homogeneity of an ionic state maintained was applied using the spray drying method, it found out that the manufacture method using the describing [above] spray drying method for having excelled also in the handling of precursor powder, and having excelled also in mass-production nature was the the best for composition of an active material.

[0015]

[Problem(s) to be Solved by the Invention] However, Co, nickel, etc. which are used for these active materials are a comparatively expensive metallic element, and it is a future big problem that it will be necessary to fully take into consideration the source of supply -- it is specified as the strategy matter while especially Co is expensive, and there is a limitation also in resources. That is, although the matter group of composition of betaFe 2O₄ (beta is a cation) called ferrite is widely used for the magnet, the magnetic device, the head for magnetic recording, or the magnetic-recording medium, in spite of using expensive metallic elements, such as Co and nickel, with Fe as a constituent, a used thing is discarded easily and the present condition is having not accomplished the deployment of the waste.

[0016] this invention is made in order to solve this technical problem, and it aims at acquiring the manufacture method of the positive active material of uniform composition, and the positive active material which can obtain it with sufficient mass-production nature easily using a ferrite. Moreover, it aims at obtaining the rechargeable lithium-ion battery which has the outstanding property using the above-mentioned positive active material.

[0017]

[Means for Solving the Problem] The manufacture method of the 1st positive active material concerning this invention is the following general formula AFe 2O₄ (the inside of a formula and A are Mn, Fe, Zn, Co, nickel, or Cr).

The solution which dissolved the multiple oxide which comes out and makes a principal component composition shown, and the mineral salt containing a lithium ion, The mineral salt containing the metallic element ion of ** a kind of 1st at least of Co, nickel, Mn, and the Fe(s), The process which obtains the solution which mixed a lithium and the 1st metallic element of the above, and the complexing agent that forms a complex so that the ratio of a lithium ion and the metallic element ion of the above 1st might be set to 1:x (0.5<=x<=1.0), It is the method of giving the process which removes

the solvent of the above-mentioned solution by spray drying, and obtains a precursor, and the process which heat-treats the above-mentioned precursor.

[0018] The mineral salt in which the manufacture method of the 2nd positive active material concerning this invention contains a lithium ion in the manufacture method of the 1st positive active material of the above is the method of a lithium nitrate, lithium sulfate, a lithium chloride, lithium fluoride, an acetic-acid lithium, or a lithium hydroxide.

[0019] The mineral salt in which the manufacture method of the 3rd positive active material concerning this invention contains the 1st metallic element ion in the above 1st or the manufacture method of the 2nd positive active material is the method of a nitrate, a sulfate, a chloride, acetate, a fluoride, or a hydroxide.

[0020] In the above 1st or the manufacture method of one positive active material of the 3rd, the complexing agent of the manufacture method of the 4th positive active material concerning this invention is the method of oxalic acid, a tartaric acid, a citric acid, a succinic acid, a malonic acid, or a maleic acid.

[0021] The 1st positive active material concerning this invention was obtained by the above 1st or one manufacture method of the 4th, and a principal component is shown by the following general formula LiMxO_2 (M is Co, nickel, Mn, or Fe among a formula, and it is $0.5 \leq x \leq 1.0$).

[0022] The 2nd positive active material concerning this invention is obtained by the above 1st or one manufacture method of the 4th using the multiple oxide whose principal components are CoFe 2O₄ and NiFe 2O₄.

[0023] The 3rd positive active material concerning this invention is obtained by the above 1st or one manufacture method of the 4th using the multiple oxide whose principal component is MnFe 2O₄.

[0024] In the rechargeable lithium-ion battery with which the 1st rechargeable lithium-ion battery concerning this invention was equipped with the separator holding the nonaqueous electrolyte containing a lithium ion between the positive-active-material layer, the negative-electrode active material layer, and the above-mentioned positive electrode and a negative-electrode active material layer, the above-mentioned positive-active-material layer has the positive active material of either a claim 5 or the claim 7.

[0025]

[Embodiments of the Invention] The manufacture method of the positive active material of the gestalt operation of the 1st of the gestalt 1. this invention operation is the following general formula AFe 2O₄ (the inside of a formula and A are Mn, Fe, Zn, Co, nickel, or Cr).

The solution which dissolved the multiple oxide-(it is also called a ferrite) which comes out and makes a principal component composition shown, The mineral salt containing a lithium ion, and the mineral salt containing the metallic element (transition-metals element) ion of ** a kind of 1st at least of Co, nickel, Mn, and the Fe(s), The process which obtains the solution which mixed a lithium and the 1st metallic element of the above, and the complexing agent that forms a complex so that the ratio of a lithium ion and the metallic element ion of the above 1st might be set to 1:x ($0.5 \leq x \leq 1.0$), It is the method of giving the process which removes the solvent of the above-mentioned solution by spray drying, and obtains a precursor, and the process which heat-treats the above-mentioned precursor. Under the present circumstances, since A of the multiple oxide which has composition of AFe 2O₄ is Mn, Fe, Zn, Co, nickel, or Cr, the positive active material which has a good performance can be manufactured.

[0026] Moreover, as mineral salt containing a lithium ion, a lithium nitrate, lithium sulfate, a lithium chloride, lithium fluoride, an acetic-acid lithium, or a lithium hydroxide can be used.

[0027] Moreover, as mineral salt containing the 1st metallic element (transition-metals element) ion, a nitrate, a sulfate, a chloride, acetate, a fluoride, or a hydroxide can be used. In this case, the 1st metallic element is transition metals, such as Co, nickel, Mn, Fe, etc. which are mainly the constituent of an active material, and what added other metals for the improvement in a property is contained. As the above-mentioned metallic element by which addition is carried out, already very many things, such as aluminum, Ti, Mg, Zn, V, Ba, Mg, Sr, calcium, etc. of a minute amount, are proposed.

[0028] Moreover, as a complexing agent, it is water-soluble, and a thing with the hydroxyl group or

carboxyl group which forms easily a lithium ion and transition-metals ion, and a complex is desirable, and can use organic acids, such as oxalic acid, a tartaric acid, a citric acid, a succinic acid, a malonic acid, or a maleic acid. Although there are EDTA (ethylenediaminetetraacetic acid), HEDTA (hydroxy ethylenediamine triacetic acid), etc. in the complexing agent which forms a complex in others, since a nitride remains in the precursive inside-of-the-body section at the time of pyrolysis, these cause a disorder of a crystal and have the problem that a cell property falls.

[0029] Moreover, it is widely [already] well-known that the spray drying method used by this invention is a method of excelling in mass-production nature compared with the above-mentioned wet method at powder composition of ceramics etc., and if this method is used, it can compound a lot of active material precursors efficiently. Since after spray drying can collect precursors in the state of the lithium which does not contain moisture and a solvent, and the organic-acid compound complex salt of transition metals, the handling of the precursor after dryness is also very easier still for it. Moreover, 160-220 degrees C of spraying temperature of spray drying are 180-200 degrees C still more desirably. A low and a precursor have inadequate dryness and its remains and moisture absorption of water of crystallization are more remarkable than this temperature. Moreover, a reaction progresses at a stretch to the pyrolysis of the compound complex salt which will be generated if it becomes the temperature beyond this, it changes to a hygroscopic high oxide again, and the yield of a precursor falls it not only cannot attain the purpose of original homogeneous mixture, but, and handling nature also becomes remarkably bad. Moreover, finally a good active material is obtained with the atomizing pressure of spray drying being 0.5-2.0Pa.

[0030] After dissolving it, when the active material was manufactured as mentioned above using the ferrite which became waste as a source of supply of elements, such as Co, nickel, Mn, Fe, etc. which constitute an active material, according to the manufacture method of the positive active material of the gestalt operation of the 1st of this invention, the active material for positive electrodes which has a good property was obtained. Moreover, it newly found out that Fe which is the constituent of a ferrite was not what checks the performance of an active material etc.

[0031] That is, supplying a part of constituent of an active material using the dissolution solution of the oxide which already became a product called a ferrite, forming a compound complex by the complexing agent, and maintaining the homogeneous ion mixed state by this compound complex according to the gestalt of this operation, a solvent is removed momentarily, and an active material precursor can be obtained without receiving the bad influence of the moisture in the moisture and solvent with which the precursive inside-of-the-body section remains, or air. By calcinating this precursor, a highly efficient active material can be obtained and a highly efficient cell property can be attained.

[0032] Moreover, since the above-mentioned precursor is extremely rich in homogeneity and impurity components, such as moisture and a solvent, do not remain inside, it excels in reactivity and 50 degrees C - about 150 degrees C of burning temperature in low temperature become possible compared with baking by the usual dry process. Furthermore, possible, by the bird clapper, reduction of burning temperature can prevent dispersing, while the lithium component of an active material calcinates, can obtain the ideal active material in accordance with the stoichiometry, and leads to improvement in a cell property. However, the burning temperature of an active material changes with kinds of active material, and although it is 600-850 degrees C in general, this temperature requirement does not restrict in this invention.

[0033] The size of the active material obtained is arbitrarily controllable by adjusting the boiling point of a spraying solution, spraying temperature, an atomizing pressure, the diameter of a two fluid nozzle, etc. However, it is not necessary to give a limit to the configuration and particle size of an active material which were compounded in this invention also in this case, and no matter it may be what thing, it can use as an active material.

[0034] A principal component is shown by the following general formula LiM_xO_2 (M is Co, nickel, Mn, or Fe among a formula, and it is $0.5 \leq x \leq 1.0$), and the positive active material of the gestalt of operation of the 2nd of the gestalt 2. this invention of operation can be obtained by the manufacture method of the gestalt 1 operation.

[0035] Moreover, in the gestalt 1 of operation, the positive active material whose principal component is $\text{Li}(\text{Co}, \text{nickel}) \text{O}_2$ can be similarly obtained using the multiple oxide whose principal components are CoFe_2O_4 and NiFe_2O_4 .

[0036] Moreover, in the gestalt 1 of operation, the positive active material whose principal component is LiMn_2O_4 can be similarly obtained using the multiple oxide whose principal component is MnFe_2O_4 .

[0037] Moreover, in the gestalt of the above-mentioned implementation, if it is excellent in positive-electrode capacity if the ranges of the 1st metallic element which forms a lithium and a multiple oxide are 0.5-1.0 in a mole ratio, and it exceeds less than 0.5 and 1.0 to a lithium, capacity will fall.

[0038] Gestalt 3. drawing 1 of operation is the block diagram of a common rechargeable lithium-ion battery, and is set to drawing. As for a negative-electrode active material layer and 7, the gasket with which a positive-active-material layer and 2 consist in 1, and a positive-electrode case and 4 consist of an insulating material in a positive-electrode charge collector and 3, the separator holding the nonaqueous electrolyte in which 5 contains a lithium ion, and 6 are [a negative-electrode charge collector and 8] negative-electrode cases. It is what was equipped with the separator 5 holding the nonaqueous electrolyte containing a lithium ion between the positive-active-material layer 1 and the negative-electrode active material layer 6, and the above-mentioned positive-active-material layer 1 has the positive active material of the gestalt 2 of the above-mentioned implementation in the gestalt of this operation.

[0039]

[Example] A detailed example is explained below.

The solution which dissolved this in the hydrochloric acid by the concentration of 0.1 M/l was adjusted using CoFe_2O_4 as an example 1. ferrite. Subsequently, the tartaric-acid solution which adjusted the lithium nitrate, and the powder and tartaric acid of a cobalt nitrate so that it might become the concentration of 0.2 M/l, respectively was produced. Predetermined volume [every] weighing capacity was carried out, and solution mixture of these was carried out so that it might become the stoichiometry of an active material LiCoO_2 . After agitating for 30 minutes as it is, spray drying was performed using the spray dryer. For spraying of a liquid, the liquid was sent at the speed of 100ml/m using the two fluid nozzle which used the compressed air together, and it sprayed by the pressure of 2.0MPa. Spraying temperature was made into 200 degrees C, and obtained the active material precursor with 95% or more of yield.

[0040] The precursor powder after dryness was put in the quartz boat, it calcinated at 800 degrees C among the atmosphere for 10 hours, and dark-brown powder was obtained. It checked that the active material obtained according to the example of this this invention was LiCoO_2 by which Fe was added according to the X diffraction.

[0041] Next, the lithium secondary battery shown in drawing 1 was manufactured using the active material obtained as mentioned above. the inside of the glove box in argon atmosphere -- this active material -- as 90wt(s)% and electric conduction material -- acetylene black of 3.0 micrometers of mean particle diameters -- as a 5wt(s)% and binding material (binder) component -- a polyvinylidene fluoride (PVDF) -- 5wt(s)% -- weighing capacity was carried out, and this was mixed with N-methyl pyrrolidone (NMP) used as a solvent, and it considered as the paste After applying this on the aluminum foil which serves as the positive-electrode charge collector 2 by the doctor blade method and carrying out a vacuum drying in 150-degree C oven, it pressed and considered as the positive-active-material layer 1.

[0042] The negative-electrode active material layer 6 was filled up with the negative-electrode charge collector 7 at the negative-electrode case 8 using the metal lithium. After infiltrating this into the separator 5 made from polypropylene (PP) to the electrolytic solution using the mixed solution of ethylene carbonate (EC)/1, and 2-dimethoxyethane (DME) / 1.0M lithium perchlorate, it inserted between the negative-electrode active material layer 6 and the positive-active-material layer 1, and put into the positive-electrode case 3 with the positive-electrode charge collector 2, and the coin type cell which closes with a gasket 4 and is shown in above-mentioned drawing 1 was produced. Let this coin cell be Sample A.

[0043] Using this cell, charge-and-discharge measurement is performed in the constant-current mode of

current density 0.1 mA/cm², and a result is shown in Table 1. However, charge voltage made 4.2V the upper limit.

[0044]

[Table 1]

	実施例		比較例			
	放電容量 (mAh/g)		放電容量 (mAh/g)			
1	A	1 6 7	R 1	1 3 8	R F 1	1 4 0
2	B	1 9 5	R 2	1 5 5	R F 2	1 5 2
3	C	1 9 0	R 3	1 6 8	R F 3	1 6 7
4	D	1 4 0	R 4	1 2 4	R F 4	1 2 5
5	E	1 9 1	R 5	1 5 9	R F 5	1 5 6
6	F	1 3 7	R 6	1 1 9	R F 6	1 1 1

[0045] The solution which dissolved this in the hydrochloric acid by the concentration of 0.1 M/l was adjusted using NiFe 2O₄ as an example 2. ferrite. Subsequently, the citric-acid solution which adjusted the acetic-acid lithium, the nickel acetate, and the citric acid so that it might become the concentration of 0.2M, respectively was produced. Predetermined volume [every] weighing capacity was carried out, and solution mixture of this was carried out so that it might become the stoichiometry of an active material LiNiO₂. As it is, it agitated for 30 minutes, and spray drying was performed like the example 1 using the spray dryer. For spraying of a liquid, the liquid was sent at the speed of 100ml/m using the two fluid nozzle which used the compressed air together, and it sprayed by the pressure of 1.5MPa. Spraying temperature was made into 190 degrees C, and obtained the active material precursor with 95% or more of yield.

[0046] The precursor powder after dryness was put in the quartz boat, it calcinated at 700 degrees C among oxygen for 10 hours, and dark-brown powder was obtained. When the active material obtained according to the example of this this invention was identified with X diffraction equipment, it checked that it was LiNiO₂ by which Fe was added.

[0047] A coin type cell is produced like an example 1 using this active material (let this coin cell be Sample B.), charge-and-discharge measurement is performed by the same measuring method, and a result is shown in Table 1.

[0048] The solution which dissolved these in the mixed acid of a hydrochloric acid and a nitric acid by the concentration of 0.1 M/l, respectively was adjusted using the powder of NiFe 2O₄ and CoFe 2O₄ as an example 3. ferrite. Subsequently, the solution which adjusted a lithium chloride, a cobalt chloride, a nickel chloride, and oxalic acid so that it might become the concentration of 0.2M, respectively was produced. Predetermined volume weighing capacity was carried out and solution mixture of this was carried out so that it might become the stoichiometry of active material LiCo_{0.2}nickel 0.8O₂. After agitating for 30 minutes as it is, spray drying was carried out like the example 1. Spraying temperature was made into 220 degrees C, and obtained the active material precursor with 95% or more of yield.

[0049] The precursor powder after dryness was put in the quartz boat, it calcinated at 750 degrees C among the atmosphere for 10 hours, and dark-brown powder was obtained. When the active material obtained according to the example of this this invention was identified with X diffraction equipment, it checked that it was LiCo_{0.2}nickel 0.8O₂ with which Fe was added.

[0050] A coin type cell is produced by the same method as an example 1 using this active material (let this coin cell be Sample C.), charge-and-discharge measurement is performed by the same measuring method, and a result is shown in Table 1.

[0051] Made this into the anode plate, used platinum for cathode, using 2OMnFe₄ magnet as an

example 4. ferrite, it was made to electrolyze and dissolve in diluted hydrochloric acid, and the solution with a concentration of 0.1M [1.] was adjusted. Subsequently, lithium sulfate, manganese nitrate, and the malonic acid were adjusted so that it might become the concentration of 0.2M, and each solution was produced. Next, predetermined volume weighing capacity was carried out and solution mixture of this was carried out so that it might become the stoichiometry of an active material LiMn_2O_4 . After agitating for 30 minutes as it is, spray drying was carried out like the example 1. Spraying temperature was made into 180 degrees C, and obtained the active material precursor with 95% or more of yield. [0052] The precursor powder after dryness was put in the quartz boat, it calcinated at 800 degrees C among the atmosphere for 10 hours, and dark-brown powder was obtained. When the active material obtained according to the example of this this invention was identified with X diffraction equipment, it checked that it was LiMn_2O_4 by which Fe was added.

[0053] A coin type cell is produced by the same method as an example 1 using this active material (let this coin cell be Sample D.), charge-and-discharge measurement is performed by the same measuring method, and a result is shown in Table 1.

[0054] The solution which dissolved in the mixed acid which used this in the example 3 by the concentration of 0.1 M/l was adjusted using 2Fe_4 rod as an example 5. ferrite (nickel, Zn). Subsequently, the lithium hydroxide was adjusted so that it might become the concentration of 0.2M, and solution was produced. Next, the nickel hydroxide of 0.2M was dissolved in the citric-acid solution adjusted to the concentration of 0.2M, and the citric-acid solution containing nickel ion was adjusted. And predetermined volume weighing capacity was carried out and solution mixture was carried out so that it might become the stoichiometry of an active material LiNiO_2 about both. After agitating for 30 minutes as it is, spray drying was carried out like the example 1. Spraying temperature was made into 210 degrees C, and obtained the active material precursor with 95% or more of yield.

[0055] The precursor powder after dryness was put in the quartz boat, it calcinated at 700 degrees C among oxygen for 10 hours, and dark-brown powder was obtained. When the active material obtained according to the example of this this invention was identified with X diffraction equipment, it checked that it was LiNiO_2 by which Fe and Zn were added.

[0056] A coin type cell is produced by the same method as an example 1 using this active material (let this coin cell be Sample E.), charge-and-discharge measurement is performed by the same measuring method, and a result is shown in Table 1.

[0057] The solution which dissolved this in the hydrochloric acid by the concentration of 0.1 M/l was adjusted using 2Fe_4 powder as an example 6. ferrite (Mn, Zn). Subsequently, the succinic-acid solution which adjusted a lithium nitrate, manganese nitrate, and the succinic acid so that it might become the concentration of 0.2M, respectively was produced. Predetermined volume [every] weighing capacity was carried out, and solution mixture of this was carried out so that it might become the stoichiometry of an active material LiMn_2O_4 . After agitating for 30 minutes as it is, spray drying was performed like the example 1. Spraying temperature was made into 220 degrees C, and obtained the active material precursor with 95% or more of yield.

[0058] The precursor powder after dryness was put in the quartz boat, it calcinated at 800 degrees C among the atmosphere for 10 hours, and dark-brown powder was obtained. When the active material obtained according to the example of this this invention was identified with X diffraction equipment, it checked that it was LiMn_2O_4 by which Fe and Zn were added.

[0059] A coin type cell is produced by the same method as an example 1 using this active material (let this coin cell be Sample F.), charge-and-discharge measurement is performed by the same measuring method, and a result is shown in Table 1.

[0060] According to the dry process which is most general manufacturing method of the example of comparison 1. former, specified quantity weighing capacity of a lithium carbonate and the cobalt oxide was carried out so that it might become the stoichiometry of the active material of an example 1, and it mixed with the ball mill for 2 hours. Next, this was put in the quartz boat, it calcinated at 900 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample r1.) was obtained. Moreover, apart from this, according to the conventional wet method, into the ferrite

solution adjusted in the example 1, the powder of a lithium carbonate and cobalt oxide was dried after mixing, mixing and dissolving so that it may become the stoichiometry of the active material of an example 1, this was packed at the quartz boat, it calcinated at 900 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample rf1.) was obtained.

[0061] A coin type cell is produced by the same method as an example 1 using these two sorts of active materials (r1, rf1) (let this coin cell be samples R1 and RF1, respectively.), charge-and-discharge measurement is performed by the respectively same measuring method, and a result is shown in Table 1.

[0062] According to the dry process which is the conventional most general manufacturing method like the example 1 of example of comparison 2. comparison, specified quantity weighing capacity of a lithium carbonate and the nickel hydroxide was carried out so that it might become the stoichiometry of the active material of an example 2, and it mixed with the ball mill for 2 hours. Next, this was put in the quartz boat, it calcinated at 800 degrees C among oxygen for 10 hours, and dark-brown active material powder (let this be a sample r2.) was obtained. Moreover, apart from this, according to the conventional wet method, into the ferrite solution adjusted in the example 2, the powder of a lithium carbonate and nickel hydroxide was dried after mixing, mixing and dissolving so that it may become the stoichiometry of the active material of an example 2, this was packed at the quartz boat, it calcinated at 800 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample rf2.) was obtained.

[0063] A coin type cell is produced by the same method as an example 1 using these two sorts of active materials (r2, rf2) (let this coin cell be samples R2 and RF2, respectively.), charge-and-discharge measurement is performed by the respectively same measuring method, and a result is shown in Table 1.

[0064] According to the dry process which is most general manufacturing method of the example of comparison 3. former, specified quantity weighing capacity of a lithium carbonate, nickel hydroxide, and the cobalt hydroxide was carried out so that it might become the stoichiometry of the active material of an example 3, and it mixed with the ball mill for 2 hours. Next, this was put in the quartz boat, it calcinated at 850 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample r3.) was obtained. Moreover, apart from this, according to the conventional wet method, into the ferrite solution adjusted in the example 3, the powder of a lithium carbonate, and nickel hydroxide and cobalt hydroxide was dried after mixing, mixing and dissolving so that it may become the stoichiometry of the active material of an example 3, this was packed at the quartz boat, it calcinated at 850 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample rf3.) was obtained.

[0065] A coin type cell is produced by the same method as an example 1 using these two sorts of active materials (r3, rf3) (let this coin cell be samples R3 and RF3, respectively.), charge-and-discharge measurement is performed by the respectively same measuring method, and a result is shown in Table 1.

[0066] Specified quantity weighing capacity of an example of comparison 4. lithium nitrate and the manganese nitrate was carried out, in addition to the ion exchange water measured so that each ion might be set to 0.2M, this was dissolved, and the mixed solution was obtained so that a lithium and manganese ion might serve as a stoichiometry of the active material of an example 4. It heated agitating this solution violently with a magnetic stirrer, and condensed by having evaporated the solvent, and the precursor was obtained. After taking this out and performing the vacuum drying of 2 hours at 200 degrees C, the quartz boat was stuffed, it calcinated at 850 degrees C among the atmosphere for 10 hours, and dark-brown powder (let this be a sample r4.) was obtained. Moreover, apart from this, according to the conventional wet method, into the ferrite solution adjusted in the example 4, the powder of a lithium nitrate and manganese nitrate was dried after mixing, mixing and dissolving so that it may become the stoichiometry of the active material of an example 4, this was packed at the quartz boat, it calcinated at 850 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample rf4.) was obtained.

[0067] A coin type cell is produced by the same method as an example 1 using these two sorts of active materials (r4, rf4) (let this coin cell be samples R4 and RF4, respectively.), charge-and-discharge measurement is performed by the respectively same measuring method, and a result is shown in Table 1.

[0068] Specified quantity weighing capacity of an example of comparison 5. lithium nitrate and the nickel nitrate was carried out, in addition to the ion exchange water measured so that each ion might be set to 0.2M, this was dissolved, and the mixed solution was obtained so that a lithium and nickel ion might serve as a stoichiometry of the active material of an example 5. The citric-acid solution furthermore adjusted to this solution 0.2M was added. The solvent was evaporated and this was made to gel over 48 hours using a rotating evaporator under reduced pressure of 1000Pa with 60-degree-C water bath. After taking this out and performing the vacuum drying of 2 hours at 200 degrees C, the quartz boat was stuffed, it calcinated at 750 degrees C among the atmosphere for 10 hours, and dark-brown powder (let this be a sample r5.) was obtained. Moreover, apart from this, according to the conventional wet method, into the ferrite solution adjusted in the example 5, the powder of a lithium nitrate and nickel nitrate was dried after mixing, mixing and dissolving so that it may become the stoichiometry of the active material of an example 5, this was packed at the quartz boat, it calcinated at 750 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample rf5.) was obtained.

[0069] A coin type cell is produced by the same method as an example 1 using these two sorts of active materials (r5, rf5) (let this coin cell be samples R5 and RF5, respectively.), charge-and-discharge measurement is performed by the respectively same measuring method, and a result is shown in Table 1.

[0070] Specified quantity weighing capacity of an example of comparison 6. acetic-acid lithium and the manganese acetate was carried out, in addition to the ion exchange water measured so that each ion might be set to 0.2M, this was dissolved, and the mixed solution was obtained so that a lithium and manganese ion might serve as a stoichiometry of the active material of an example 6. The ethylene glycol solution furthermore adjusted to this solution 0.4M was added. It heated agitating this violently in a 90-degree C water bath, the solvent was evaporated, and polymerization reaction was advanced over 24 hours. After taking this out and performing the vacuum drying of 2 hours at 150 degrees C, the quartz boat was stuffed, it calcinated at 850 degrees C among the atmosphere for 10 hours, and dark-brown powder (let this be a sample r6.) was obtained. Moreover, apart from this, according to the conventional wet method, into the ferrite solution adjusted in the example 6, an acetic-acid lithium and the powder of manganese acetate were dried after mixing, mixing and dissolving so that it may become the stoichiometry of the active material of an example 6, this was packed at the quartz boat, it calcinated at 850 degrees C among the atmosphere for 10 hours, and dark-brown active material powder (let this be a sample rf6.) was obtained.

[0071] A coin type cell is produced by the same method as an example 1 using these two sorts of active materials (r6, rf6) (let this coin cell be samples R6 and RF6, respectively.), charge-and-discharge measurement is performed by the respectively same measuring method, and a result is shown in Table 1.

[0072] According to Table 1, it turns out that the positive active material of examples 1-6 has high service capacity rather than which thing of the example of comparison. Moreover, even if Fe, or Fe and Zn were contained in the above-mentioned active material, not having a bad influence on service capacity was shown.

[0073] Furthermore, combination was selected except the object which A of the multiple oxide which has composition of AFe_2O_4 used in the examples 1-6 among Mn, Fe, Zn, Co, nickel, or Cr, and comparison investigation of those service capacity was respectively conducted like the examples 1-6 of this invention, and the examples 1-6 of comparison. Consequently, it was shown that the direction of the positive active material of this invention has [as for service capacity / in all cases] high capacity like the above in 10 - 30 mAh/g.

[0074]

[Effect of the Invention] The manufacture method of the 1st positive active material of this invention is the following general formula AFe_2O_4 (the inside of a formula and A are Mn, Fe, Zn, Co, nickel, or Cr).

The solution which dissolved the multiple oxide which comes out and makes a principal component composition shown, and the mineral salt containing a lithium ion, The mineral salt containing the metallic element ion of ** a kind of 1st at least of Co, nickel, Mn, and the Fe(s), The process which obtains the solution which mixed a lithium and the 1st metallic element of the above, and the complexing agent that forms a complex so that the ratio of a lithium ion and the metallic element ion of the above 1st might be set to 1:x ($0.5 \leq x \leq 1.0$), It is effective in the ability to obtain with sufficient mass-production nature easily using a ferrite by the method of giving the process which removes the solvent of the above-mentioned solution by spray drying, and obtains a precursor, and the process which heat-treats the above-mentioned precursor.

[0075] In the manufacture method of the 1st positive active material of the above, the mineral salt containing a lithium ion is the method of a lithium nitrate, lithium sulfate, a lithium chloride, lithium fluoride, an acetic-acid lithium, or a lithium hydroxide, and the manufacture method of the 2nd positive active material of this invention is effective in the ability to obtain with sufficient mass-production nature easily using a ferrite.

[0076] In the above 1st or the manufacture method of the 2nd positive active material, the mineral salt containing transition-metals element ion is the method of a nitrate, a sulfate, a chloride, acetate, a fluoride, or a hydroxide, and the manufacture method of the 3rd positive active material of this invention is effective in the ability to obtain with sufficient mass-production nature easily using a ferrite.

[0077] In the above 1st or the manufacture method of one positive active material of the 3rd, a complexing agent is the method of oxalic acid, a tartaric acid, a citric acid, a succinic acid, a malonic acid, or a maleic acid, and the manufacture method of the 4th positive active material of this invention is effective in the ability to obtain with sufficient mass-production nature easily using a ferrite.

[0078] It is obtained by the above 1st or one manufacture method of the 4th, a principal component is shown by the following general formula LiM_xO_2 (M is Co, nickel, Mn, or Fe among a formula, and it is $0.5 \leq x \leq 1.0$), and the 1st positive active material of this invention is effective in composition being homogeneous.

[0079] The principal component was obtained by the above 1st or one manufacture method of the 4th using the multiple oxide which are $CoFe_2O_4$ and $NiFe_2O_4$, and the 2nd positive active material of this invention is effective in composition being homogeneous.

[0080] The principal component was obtained by the above 1st or one manufacture method of the 4th using the multiple oxide which is $MnFe_2O_4$, and the 3rd positive active material of this invention is effective in composition being homogeneous.

[0081] In the rechargeable lithium-ion battery equipped with the separator holding the nonaqueous electrolyte containing a lithium ion between the positive-active-material layer, the negative-electrode active material layer, and the above-mentioned positive electrode and a negative-electrode active material layer, the above-mentioned positive-active-material layer has the positive active material of the above 1st or either of the 3rd, and the 1st object for the rechargeable lithium-ion batteries of this invention is effective in a property being excellent.

[Translation done.]

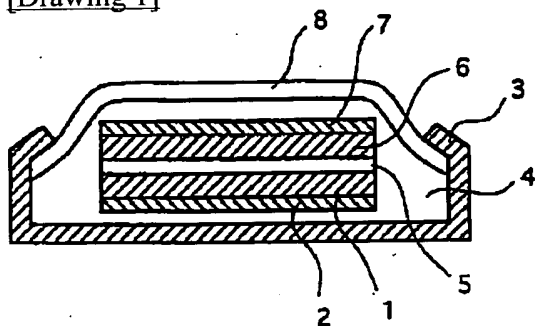
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DRAWINGS

[Drawing 1]



- 1: 正極活性物質層
- 2: 正極集電体
- 5: セパレータ
- 6: 負極活性物質層
- 7: 負極集電体

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the block diagram of a common coin cell.

[Description of Notations]

1 A positive-active-material layer, 2 A positive-electrode charge collector, 5 Separator, 6 A negative-electrode active material layer, 7 negative-electrode charge collector.

[Translation done.]